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Selective ultra-trace atmospheric passive sampling of gaseous perfluoroalkyl carboxylic acids†

Eric Vanhauwaert,[a] Lindy Carmichael,[a] Irina Nistorescu,[a] Leigh R. Crilley, [iD] ‡[a] Chubashini Shunthirasingham,[b] Hayley Hung,[b] Cora J. Young [iD] *[a] and Trevor C. VandenBoer [iD] *[a]

Acidic pollutants have long been known to have detrimental impacts on remote ecosystems. They have been subject to assessment through long-term monitoring with low cost methodologies, such as passive sampling. Atmospheric oxidation is becoming recognized as a source of persistent perfluorinated carboxylic acids (PFCAs) derived from volatile poly- and perfluorinated alkyl substance (PFAS) precursors. In this work, nylon substrate passive air samplers that are selective for atmospheric acids are described. Their PFCA suitability is verified through extensive quality assurance and control tests, including controlled chamber tests for sampling rates. The sampling rate for gaseous trifluoroacetic acid (TFA; C2) is established experimentally, with ultra-trace detection limits at parts per quadrillion by volume mixing ratios (ppqv; 10^{-15} mol mol^{-1}) for a sampling period of one week. Sampling rates for the C3–C6 homologues of the PFCA family were then derived from two diffusion theories of varying complexity. Proof-of-concept measurements were performed at urban, rural continental, and remote marine sites in Canada for over a year. All PFCA homologues from C2–C6 were detected above the method detection limits, with abundance decreasing with increasing chain length and from urban to rural to remote locations. Atmospheric abundance was dominated by TFA, which also showed trends consistent with known sources of precursors and atmospheric oxidation chemistry. This new PFCA-specific passive air sampling method represents a promising new option for the study of PFCA formation, transport, and fate in the atmosphere.

Environmental significance

Perfluoroalkyl carboxylic acids (PFCAs) are persistent and mobile in aquatic systems. The production and global dispersion of these molecules is understudied in the atmosphere due to a lack of validated sampling techniques that can be widely deployed. A robust and cost-effective passive air sampling technique was developed to measure the distribution of gaseous atmospheric PFCAs at three locations across Canada over a year. Trifluoroacetic acid was the most abundant and showed summer enhancement due to known precursor emissions and atmospheric chemistry.

1. Introduction

Perfluoroalkyl carboxylic acids (PFCAs), a sub-class and terminal degradation products of per- and polyfluoroalkyl substances (PFAS), are pollutants in the environment that are known to be persistent. Unique properties of PFAS, such as their hydrophobicity, lipophobicity, thermal stability, and resistance to various chemical agents, have resulted in their production for use in a variety of commercial products.[1] As a consequence,

environmental PFCAs originate from direct emissions through their use as processing aids[2,3] and indirect degradation of precursor PFAS.[4,5]

PFCAs have been found ubiquitously in the global environment, even though they are not naturally occurring.[6–8] Their chemical stability prevents their degradation under typical environmental conditions and arguments have been made that PFCAs have exceeded their planetary boundary.[9,10] Atmospheric formation of PFCAs is recognized as an important pathway for global contamination.[5,11–13] The atmospheric abundance of PFCAs over long temporal and across wide spatial scales are of high importance, and demand accurate atmospheric measurements with methods that can be easily adopted by the global community of researchers.[14,15]

Passive air samplers (PAS) have been employed for many years to provide an inexpensive and power-free sampling

[a] Department of Chemistry, York University, Toronto, M3J 1P3, Canada. E-mail: youngcj@yorku.ca; tvandenb@yorku.ca

[b] Air Quality Processes Research Section, Environment and Climate Change Canada, Toronto, M3H 5T4, Canada

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method.[16,17] These features make them suitable for deployment in challenging to access remote areas and in large numbers. Thus, PAS are able to capture wide spatial scale changes in environmental concentrations, albeit at days to months temporal resolution. The functional principle of PAS is to retain analytes of interest with a collection medium,[16] which occurs either due to the analytes preferentially partitioning into it, on to it, or by a more selective reactive uptake process.[16,18]

A few studies have explored the use of PAS for sampling the sum of gaseous and particulate PFCAs in air with polyurethane foam disks (PUF), different types of porous divinylbenzene and polystyrene resin (XAD), or a combination of both.[19,20] The sorption of PFCAs onto PUF has generally been found to be low, reaching partitioning equilibrium for most compounds after just one day.[20] Although the addition of XAD embedded resin improves performance by approximately two orders of magnitude, several challenges remain.[20] A linear sampling uptake has only observed over a few weeks, limiting usefulness for sampling at monthly to annual timescales.[20] Additionally, the PUF or PUF–XAD combination requires extensive sample preparation involving hours of Soxhlet extraction from the PUF and XAD using organic solvents, and further time concentrating the extract using rotary evaporation.[21] Method development of PAS has not yet considered the emerging importance of ultra-short-chain PFCAs, such as trifluoroacetic acid (TFA) and perfluoropropionic acid (PFPrA), which are present in atmospheric and deposition samples at much higher levels than PFCAs with 4 carbon atoms or more ($\geq$C4).[21–25] Thus, an increasing need of the scientific community is for a more selective passive air sampler method to address these challenges. An attractive avenue worth considering is one which takes advantage of the acidic properties of PFCAs which have not been selectively targeted by passive air sampling methods to date.

Nylon-based PAS established as effective collectors of atmospheric acids, whether abundant or ultra-trace in quanty. The suitability of nylon, a polyamide material, dates back to the 1980s when it was found to efficiently and quantitatively collect atmospheric acids such as hydrochloric acid and nitric acid (HNO_3).[26,27] Since then, nylon with highly controlled porosity and thickness has been used as a collection medium in PAS, mostly for the collection of gaseous HNO_3.[17,28–30] Unlike PUF–XAD-based PAS, the extraction procedure for nylon-based PAS is not only fast and simple but the nylon sorbents have been shown to be reusable.[17,31] The sampling rates are also possible to calibrate.[28] They have been deployed in remote regions, where they measured gaseous HNO_3 at mixing ratios as low as 9 parts per trillion (10^{-12} mol mol^{-1}, pptv) during a 35-day sampling period, with the potential to detect lower values if deployed longer, demonstrative of their ultra-trace capabilities.[17] Considering that gaseous PFCAs are strong atmospheric acids and found at ultra-trace levels, nylon-based PAS present a promising new option to study the atmospheric chemistry and transport of PFCAs. With recent developments in generating known gas phase quantities of PFCAs alongside a chemically selective passive air sampling medium,[32,33] more reliable and accurate measurements of their atmospheric abundance should be possible to obtain from direct calibrations performed in atmospheres of known composition.

Primary standard calibration is particularly important, as no atmospheric sampling technique for PFCAs has undergone formal validation to date and existing measurement approaches rely heavily on method intercomparisons.

Calibration of gas-phase samplers can be performed by controlled chamber experiments and/or orthogonal chemical measurement techniques deployed in the field, where independent measurements of a compound use fundamentally different sampling and/or detection techniques. Controlled chamber calibrations of nylon passive samplers have reliable uptake sampling rates (commonly referred to as dose–response rates) for HNO_3. This approach allows a robust calibration of the nylon across the dynamic range of expected environmental concentrations, whereas field-derived rates are heavily dependent on the composition of ambient air. Annular denuders have been used as an orthogonal sampling technique to calibrate nylon-based PAS for gas-phase HNO_3, both in an atmospheric chamber and in the field.[17,28] Denuders have also been used to quantify gas-phase PFCAs based on their chemically-explicit selectivity for acids, a property which has been standard practice by monitoring agencies for strong acids for decades.[34] They have not yet been fully validated for PFCAs through controlled experiments.[35,36] Despite this, annular denuders are currently the best active sampling option for quantitatively collecting gaseous PFCAs that avoids sampling biases of other commonly used active sampling techniques.[15,35]

The goal of this work is to validate the use of nylon PAS for PFCAs in the gas phase by calibrating the PAS. To do so, we validate an extraction method, which is then paired with established quantitative techniques. Spike and recovery, internal standards, and a variety of blanks were evaluated for the PAS analytical method steps to ensure efficient extraction and quantitation of PFCAs, and for prevention of contamination/bias. A sampling rate calibration was conducted for TFA using an atmospheric chamber with gas mixtures controlled by a permeation device and zero-air generator. The sampling rate of other PFCAs was then predicted by extension from TFA using Graham and Fuller's Laws for diffusion.[17,37] The resulting method provided a validated PAS approach for TFA in the gas phase and a reliable framework for application to atmospheric PFCAs with carbon chain lengths up to C6. Thus, a suite of PAS was deployed in replicate at urban, semi-urban, and remote Canadian locations that include continental and coastal sites. Deployments of weeks to months were typical when detecting C2–C6 PFCAs, but total durations of up to a year were possible in the remote atmosphere where sites were difficult to access and the total atmospheric acid abundance is known to be low. We show that this technique overcomes many of the current challenges for gas phase PFCA measurements such as selectivity, ultra-trace detection limits, dynamic range, sampling site selection, maintenance requirements, and minimizing costs.

2. Methods

2.1 Chemicals and materials

Sodium carbonate (Na_2CO_3) (>99.5%), glycerol (>99%), dichloromethane (DCM; ACS reagent Grade) and sodium

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hydroxide stock solution (NaOH; 49–51% in deionised water) were obtained from Sigma-Aldrich. Methanol (MeOH) of both HPLC and Optima LC-MS grades were obtained from Fisher Chemical. Trifluoroacetic acid (TFA; HPLC grade) was purchased from EMD Millipore (MA, US); PFPrA, perfluorobutanoic acid (PFBA) and perfluoropentanoic acid (PFPeA, >97%) were purchased from Sigma-Aldrich (MO, US); and perfluorohexanoic acid (PFHxA, >97%) from Synquest (FL, US). The sodium salts of TFA (>98%) and PFPrA (>99%) were obtained from Sigma-Aldrich. Stock solutions of PFCAs for gas chromatography-mass spectrometry (GC-MS) analysis were prepared in ethyl acetate (EtAc; HPLC Grade; Anachemia VWR, PA, US) at 500 μg mL^{-1}, which were diluted to working concentrations (0.5–250 μg L^{-1}). Mass-labeled $^{13}C_2$-TFA (>97%) was purchased from Toronto Research Chemicals; $^{13}C_3$-PFBA was purchased as a mixture with other labelled PFCAs in MeOH (2 μg mL^{-1}; MPFAC-C-IS) from Wellington Laboratories. These compounds were combined into one MeOH solution and used as internal standards (IS) for GC-MS analysis. Diphenyl diazomethane (DDM; >90%) was synthesized in-house using established methods[38] or purchased from Toronto Research Chemicals (ON, Canada), but at a lower purity.[25]

Stock solutions for ion chromatography with conductivity detection (IC-CD) and mass spectrometric (IC-MS) analysis were prepared in Milli-Q water at 1000 mg mL^{-1} from the sodium salts of PFCAs, which were diluted to working concentrations (5–500 μg L^{-1}), with the IC-MS calibration range being extended to lower concentrations (10–10^4 ng L^{-1}). Ultrapure Milli-Q deionised water (DIW; 18.2 MΩ cm at 25 °C) was obtained from an in-house system (Direct 8; EMD Millipore). Mass-labeled $^{13}C_1$-TFA (T786038) was purchased from Toronto Research Chemicals (ON, Canada) and dissolved in MeOH to reach a concentration of 50 mg mL^{-1}. Mass-labeled $^{13}C_4$-PFBA, $^{13}C_3$-PFPeA, and $^{13}C_2$-PFHxA were individually obtained from Wellington Laboratories (ON, Canada) and dissolved in MeOH. These mass-labeled compounds were combined into one Milli-Q water solution for use as internal standards in IC-MS analysis.

2.2 Passive air sampler components, preparation, and extraction for PFCAs

The custom-built nylon-based PAS are based on an adaptation from our previous design that was used to measure ultra-trace levels of gaseous HNO$_3$.[17] The filter pack sampler assembly
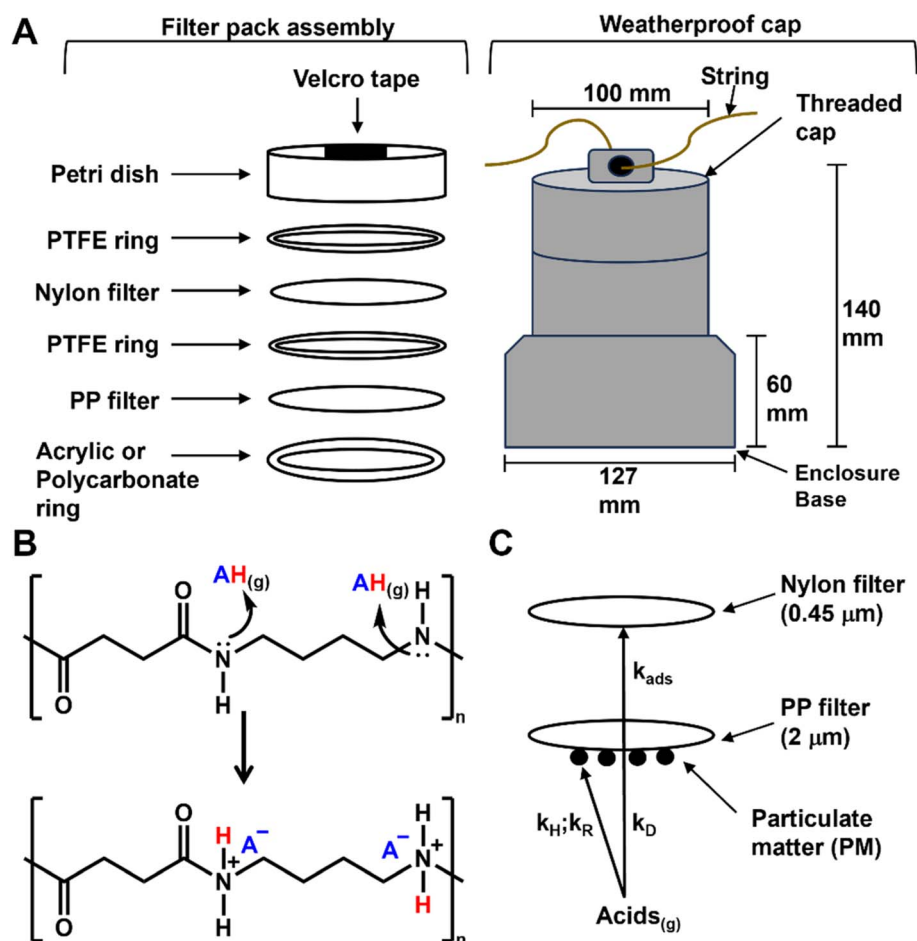

Fig. 1 (A) Passive air sampler components and assembly order prior to affixing into weatherproof cap for sampling (modified from Place *et al.*[17]); (B) proposed reactive uptake mechanism of atmospheric acids to nylon filters, where analogous reactions can take place at terminal amino groups; (C) diffusion sampling rate (k_d) controls on the rate of adsorption (k_{ads}) for quantitative collection of PFCAs by PAS may be impacted by air–water partitioning (k_H) or reactive uptake (k_R) on materials collected on the overlying filter.

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(Fig. 1A) is composed of one nylon membrane filter (47 mm diameter, 0.45 μm pore size, 115 μm thickness, Sartorius, Fisher Scientific, P/N 2500647N), one polypropylene filter (PP; 47 mm diameter, 2.0 μm pore size, 180–250 μm thickness, Tisch Scientific, SKU: SF14908), one Petri dish (60 × 15 mm, Fisher Scientific), two polyfluorotetraethylene (PTFE) rings (52 × 2 mm, McMaster Carr, P/N 8547K33), and one polycarbonate ring (53 × 4 mm, McMaster Carr, P/N 8486K541).

The PTFE and PP materials were used as inert surfaces to minimize sorption bias and are effectively cleaned between uses by our standard washing procedures. Weatherproof enclosures painted with a reflective silver coating are used to protect the filter pack assembly from atmospheric conditions (e.g. strong winds) that would cause sampling to diverge from a diffusion regime, or from precipitation interactions which could introduce contaminants and alter the sampling rate. The silvering reflects sunlight to reduce temperature differences in the filter pack assembly compared to the ambient air. Atmospheric acids, including PFCAs, ideally sorb onto the nylon filters through an acid–base reaction, with one likely mechanism illustrated in Fig. 1B in addition to reaction with any terminal amino groups. The PP filter, a deactivating material, physically blocks particles or other suspended atmospheric contaminants from reaching the nylon.

This PP barrier allows gas molecules, inclusive of acids, to permeate at a constant rate through the material pores (k_D; Fig. 1C) followed by selective chemisorption of acids. A concentration gradient between the PP and nylon filters facilitates continuous diffusion of acids to the nylon substrate. The sampling rate of acid analytes may be biased by the solubilization (k_H) or reactive uptake (k_R) of gas-phase acids to the PP filters when water or particulate matter (PM) have been accumulated (Fig. 1C).[17,28] The PP filter implemented here replaces more expensive PTFE filters previously used, with the rationale for material selection and experimental validation by ambient intercomparison provided in the ESI (Section S1).† It is likely that PP can be used to replace PTFE for the nylon filter ring supports as well. Details on our custom-made passive air sampler standard operating procedures have been revised in this work and follow below.

The washing, assembling, and extraction procedures of PAS were adapted from Place et al.[17] Our cleaning procedures for the sampler materials prevent the fluoropolymers from potentially acting as a source of PFCA contamination through release of residuals.[39,40] A new cleaning procedure for the PP filters was developed by rinsing 6 times in a 1 L PP container with DIW, soaking in DIW for 12 h, rinsing an additional 6 times, and soaking again for a minimum of 12 h. Nylon membrane filters were prepared by rinsing 6 times in a 1 L PP container with DIW, soaking for a minimum of 12 h in 15 mM of Na_2CO_3 to displace any bound acid impurities, rinsing another 6 times with DIW, and soaking in DIW again for a minimum of 12 h. Both types of filters were air dried for 2 h between two Kimtech® Kimwipes on a clean benchtop before being installed into filter pack assemblies with clean gloves and tweezers. The support rings are installed into the Petri dishes with the nylon and PP filters tightly secured between them. The PAS are then covered with

the lid of the Petrie dish, secured using tape, placed into sealed Ziploc bags, and refrigerated until deployment.

At sampling locations, including within the experimental chamber, PAS were removed from the Ziploc bags, separated from the Petri dish covers, and secured at the top of the weather shield using hook and loop fastener, as shown in Fig. 1A and S1.† The weather shields are then hung on a stable structure for the sampling period duration and the filter packs removed during collection in the reverse order. Field blanks are filter pack assemblies transported to the sampling locations, exposed to the air for 10 seconds, re-covered and placed back into the Ziploc bags for extraction alongside the atmospheric passive samples.

For extractions, 15 mL Falcon® conical tubes were pre-cleaned with six rinses of DIW and one final rinse with HPLC MeOH. Nylon filters were taken out of the filter pack assemblies with DIW-cleaned tweezers and gently rolled to transfer into the tubes. Extraction conditions were first optimized through spike and recovery experiments, which were conducted at TFA levels of 400 ng with 0–4 mM NaOH at room temperature (22 °C) and 4 °C. The optimal method for TFA (3–4 mM NaOH at either temperature) was then applied to a mixture of 0.5–100 ng of C2–C6 PFCAs, reflective of their relative and absolute abundance, to ensure quantitative recovery across the target analyte suite (Section S2 and Table S1†). Therefore, IC-CD or IC-MS analysis used 3 or 4 mL of 3–4 mM NaOH in DIW added to the tubes containing the nylon filters which were sonicated for 15 min, followed by storage in the refrigerator at 4 °C overnight with the filter left in the extraction solution (Fig. S3†). The filter was removed, an extract aliquot transferred to an autosampler vial, internal standards added (for MS only), and the sample subject to analysis. For GC-MS analysis, 4 mL of 0.1 M NaOH in Optima® methanol was added to the Falcon® conical tube containing nylon filters and sonicated for 15 min. Extraction efficiencies determined by spike and recovery (Section S2 and Table S1†) were applied for quantitative determinations in calibration chamber experiments. Since the recoveries across the homologue suite were broadly quantitative, we report the determined ambient atmospheric mixing ratios through the use of internal standards, but without recovery correction, to present conservative values.

For GC-MS analysis internal standards were added prior to sample preparation, adapted from the method of Ye et al.[25] Nylon filter extracts in 0.1 M NH_4OH in MeOH were blown down with nitrogen gas at 30 °C. The residues reconstituted in 500 μL of ethyl acetate and 500 μL DCM with ten microliters of 0.1 M DDM in DCM added to derivatize the PFCA analytes. The samples were vortexed twice for 10 s and sonicated for 15 min to promote the completion of the reaction, followed by transfer to autosampler vials for analysis.

2.3 Validation of new nylon material for acid sampling

Nylon-based PAS have been well-characterized for collecting $HNO_{3(g)}$ in the atmosphere,[17] but recently the standard material, Nylasorb, has been discontinued and alternatives needed to be identified. Thus, quality control checks were necessary to

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validate the new material in these samplers using HNO_3, in addition to a controlled calibration for TFA.

An ambient intercomparison was first undertaken to measure $HNO_{3(g)}$ in outdoor air using nylon passive sampling with filters manufactured by Sartorius (ESI; Section S3†). The new filters were deployed alongside acid-selective sodium carbonate-coated annular denuders attached to a vacuum pump. This experiment was conducted to determine whether the sampling rate of the new nylon membrane was the same or different from the previously validated Nylasorb material.[17] Three deployments were conducted between July 2020 and April 2021 on the roof of the Petrie Science and Engineering Building at York University in Toronto, Ontario, Canada (44.7738° N, 79.5071° W, 220 m above sea level). Meteorological conditions were monitored using a co-located customized Campbell Scientific weather station that included an anemometer, temperature, pressure, and relative humidity sensors (Table S2†). The annular denuder preparation procedure followed the EPA Compendium Method IO-4.2.[41] Specific details of the sampling strategy and annular denuder preparation and extraction are presented in the ESI (Section S2).†[42] Denuders were deployed in one or two medium volume active air samplers (URG-3000ABC, URG Corp, Chapel Hill, NC, USA), containing four to eight annular denuders, and 2.5 μm cutoff particulate matter cyclones to prevent sampling of aerosols with the gas, as these small particles pass through the denuders inertially by design. The flow rate for each denuder was ∼8 L min^{-1}. The first and second deployments consisted of a total of 8 denuders, while only four denuders were used to validate the determined sampling rate in the third. Field blank filter pack assemblies were exposed to outdoor air for 30 s when deploying the sampling filters. Aqueous extracts of the annular denuders were stored at 4 °C until analysis by IC (Section S3†).

2.4 Calibrating PAS with gaseous trifluoroacetic acid

To determine the sampling rate of our nylon-based PAS they need to be exposed to known quantities of gas phase PFCAs. Here we use TFA and establish its sampling rate using orthogonal measurements by annular denuders. Due to its low molecular weight, TFA is the most volatile of the PFCA suite and known to be the most abundant in the atmosphere, making this calibration ideal to pursue.[15,21–25] Calibrations were performed under controlled conditions to minimize variability in the determined sampling rate due to changes in temperature, humidity, and wind speeds. We created stable and atmospherically-relevant TFA mixing ratios and humidity using an atmospheric simulation chamber. This follows established methodology used to calibrate nylon PAS for HNO_3.[28,43] Our chamber gas handling system was developed in-house. All components are described in detail in the ESI (Section S4 and Fig. S6).† It includes a home-built zero-air generator (adapted from ref. 44) to control dilution rates and set TFA mixing ratios, a permeation device to emit a constant mass of TFA per unit of time,[45] a clean 1 m^3 perfluoroalkoxy alkane (PFA) atmospheric chamber (Welch Fluorocarbon, Inc) outfitted with two fans (Orion fans, OA4715-12TB) to keep the contents well mixed, and retort stands to affix the PAS within the chamber interior. A

simple sensor (ONA47D9XCF, Pimoroni Enviro+) inside the chamber measured relative humidity and temperature.

Methods for the preparation and extraction of denuders have been previously described in Ye et al.[25] and can be found in detail in the ESI (Section S5).† Passive samplers and denuders were analyzed using IC-CD. Full analytical details can also be found in Section S5 of the ESI.† Briefly, the IC-CD was conducted on a 300 μL sample aliquot using an anion-selective preconcentration column (5 × 23 mm, 18 μm dp, 6% DVB) followed by separation on an anion-exchange analytical column (AS23 4 × 250 mm, 6 μm dp, 55% DVB, Thermo Scientific) at a flow rate of 1 mL min^{-1} using a gradient separation.

The annular denuder was necessary to quantify gas-phase TFA within the chamber, as it was expected to undergo wall interactions (ESI; Section S6†), reducing the mixing ratio compared to using only the permeation rate.[46,47] Chamber experiments were performed at TFA mixing ratios of 135 or 373 pptv (equivalent to 0.7 and 1.9 μg m^{-3}) at 27 ± 3 °C and a relative humidity (RH) of 40 ± 5%, with sampling times varying from hours to days. In total, these experiments delivered 14 exposure levels (i.e. concentration × time) to triplicate PAS placed within the chamber for a single experiment, for a total of 42 measurements. Each chamber experiment included an annular denuder sample, for a total of 14. Combined, these were used to generate the sampling rate curve via linear regression of the mass of TFA extracted from the nylon filters (μg) relative to the time-weighted concentration of TFA present in the chamber measured by the annular denuder.

2.5 Ambient atmospheric sampling

The PAS were deployed in four locations in three areas of Canada: Saturna Island, BC; Toronto, ON (two locations); and Tadoussac, QC (Section S7 and Table S3†). Saturna Island samples were collected on a remote hilltop approximately 1 km from the coast. A single sample was collected from Dec 2021 to Dec 2022. Toronto samples were collected on the rooftop of Petrie Science and Engineering Building at York University, with five samples collected between May 2022 and June 2023. A second set of five Toronto samples was collected from a residential area between April 2022 and June 2023. Tadoussac samples were collected in a rural area approximately 750 m from the St. Lawrence River. Four samples were collected between January and October 2022. Field blanks were collected and three replicates were deployed during each period at each site, though some were lost during sampling (Table S3†). Sampling heights were at least 0.5 m above the ground. Samples were extracted and analyzed by GC-MS or IC-MS. Full IC-MS method details can be found in the ESI (Section S5).† Briefly, 750 μL of the sample was injected to an anion-selective concentrator column (5 × 23 mm, 18 μm dp, 6% DVB) and separated by anion exchange (2 × 250 mm, 7 μm dp, 55% DVB, alkanol quaternary ammonium exchanger) using a mobile phase gradient. Isotopically labelled internal standards were added to all samples prior to analysis, where each PFCA was corrected for matrix effects and instrument fluctuations, except PFPrA which used $^{13}C_4$-PFBA. This internal standard has

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a different retention time from PFPrA and may not properly account for ion suppression or enhancement that can occur for PFPrA in each sample. Thus, the quantification for PFPrA is less robust than the other PFCAs determined from this method.

3. Results and discussion

3.1 Passive sampling method innovations, quality control, and validation

Several adaptations for this sampling methodology were implemented and are briefly described here with full details provided in the ESI.† To reduce costs, the protective overlying filter of PTFE was replaced with one of PP and the resulting ambient atmosphere intercomparison of triplicate samples with each approach showed no significant difference in the collected mass. A slight increase in the observed replicate relative standard deviation was found when measuring C2–C6 PFCAs rising from 0.7 to 4.1% (Section S1†). New nylon filter materials were also assessed and were found to exhibit no change at a 95% confidence interval in the average HNO_3 sampling rate by two methods (Section S3†). However, an increase in variance between replicates with the new nylon material was observed, as the material properties are not focused on uniformity for gas phase passive sampling (Section S3†). As a result, we recommend collection of replicates at all times to ensure the precision of atmospheric abundance measurements can be reported. If future monitoring requires improved method performance, this can be readily obtained by increasing the number of replicate samples to five or more (Section S3†).

Alongside these changes, additional quality assurance (QA) and quality control (QC) tests were conducted, specifically targeting PFCAs, that have also not been previously reported for HNO_3 passive samplers (spike and recovery, field blanks) or annular denuders (field, method, analytical blanks) in order to optimize the quantitative performance of the technique. Quantitative recoveries of PFCAs from the nylon filters were obtained and handling of both apparatuses were confirmed to be analytically robust against systematic error (Section S2†).

Spiked levels at 100 and 400 ng of TFA were designed to fall within expected levels recovered from chamber experiments which spanned 50–1100 ng followed by IC-CD analysis. Lower concentration spike and recovery experiments were conducted using the IC-MS at relevant masses obtained from ambient samples, with 4 ng for TFA, 20 and 1 ng for PFPrA, and 20 and 0.5 ng for C4–C6. These were all found to yield quantitative recoveries (75–125%) using an extraction solvent of 3 mM NaOH when conducted at either 4 °C or room temperature. In the absence of a competing ion (OH^-) it was not possible to recover the analytes from the filters (<15% at either PFCA concentration level). In the presence of one recoveries increased with OH^- concentration. The best overall accuracy and precision were obtained at 3–4 mM OH^- for the PFCA analyte suite (Fig. S3†). Similar recoveries were obtained for the GC-MS method, although slightly lower due to losses arising from the additional sample preparation steps (Table S1†). Positive controls were also performed with denuder extracts by spiking them with 100 μg of TFA. The spiked denuder

extract obtained a recovery of 100.7 ± 0.4% ($n = 3$), indicating negligible bias associated with the diluted matrix.

Negative controls were performed in the form of extraction solvent and method blanks for the annular denuders, in addition to field blanks for PAS. The GC-MS extraction solvent, method, and field blanks ($n = 3$ each) were found to be below the limit of detection (LOD) for the C3–C6 PFCAs, indicating no discernible contamination arising from the PAS method and field sampling procedure. Trace levels of TFA were occasionally detected in field blanks, on the order of 1–5% of the sample mass collected, with higher relative values found where outdoor mixing ratios were low and sampling durations were short. For analysis with the IC-CD, no detectable signal of TFA or PFPrA was observed in the extraction solvent, method, or field blanks of PAS.

Overall, the QA/QC resulting from each analysis method demonstrates that PFCA contaminants from the assembling, transport, storage, and disassembling of PAS are below the detection limits of these two techniques. Therefore, signals arising from atmospheric or experimental samples collected in the lab truly reflect the exposure of the nylon substrates and their accumulation of gaseous PFCAs present in those environments.

3.2 Chamber calibration of TFA using an atmospheric chamber

The nylon-based PAS were calibrated for TFA by inserting them into a clean chamber with a known amount of gas-phase TFA measured by collection on Na_2CO_3-coated annular denuders on the chamber outflow. The hundreds of pptv (~1 μg m^{-3}) chamber levels of TFA are considered ultra-trace in the atmosphere.

Monitoring TFA in the chamber by annular denuder (μg m^{-3}) corrects the delivered quantities for chamber wall losses. The observed quantities were then multiplied by the sampling duration in the chamber (h) to obtain the sampling rate relationship (Fig. 2).[28,29,48] The TFA extracted from the nylon filter was corrected for its 83% extraction efficiency (Section S2†). The relative standard deviation between PAS triplicates within the chamber ranged from 2–30%, with 12 of the 14 triplicate sets having a relative standard deviation of 15% or below (Fig. 2). This reflects the expected consistent mixing provided by the fans within the chamber. These outcomes are consistent with the variability in calibration reported in other chamber studies for PAS, including previous calibration of nylon PAS for HNO_3.[28,29,48,49] The small negative intercept in Fig. 2 (red line) might suggest negative bias with the TFA quantified by PAS or positive bias with the TFA quantified by annular denuders.

In Section S2,† the QA/QC demonstrated that quantitative recoveries were obtained for annular denuders, with method blanks showing no detectable signal. Additionally, PAS spike and recoveries experiments achieved quantitative outcomes, the efficiency of which were corrected for in Fig. 2, also with no detectable signal in the PAS blanks. Therefore, a calibration with a non-zero intercept due to bias would not be consistent with the results of the QA/QC, as all calibration samples were above the method LOQ. An assessment of these QA/QC metrics
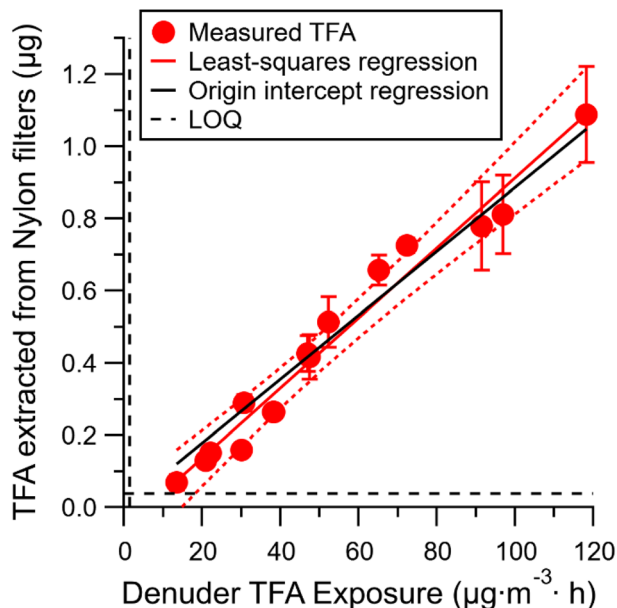
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Fig. 2 Chamber calibration of PAS for TFA. Each data point represents the mean measurement of triplicate PAS *versus* an annular denuder measurement multiplied by exposure time. The error bars are one standard deviation of triplicate PAS determinations. The sampling rate is determined using the inverse of the slope obtained by linear regression in the form $y = mx + b$ with R^2 being the coefficient of determination. Upper and lower boundaries (red dotted lines) represent the confidence bands of the linear regression at a 99.73% confidence interval of the least-squares regression slope (red line; $y = 0.0097(\pm 0.0018)x - 0.06(\pm 0.11)$, $R^2 = 0.97$). When the origin is required to be a point on the line as determined by the QA/QC results from these experiments, the regression takes the form of the black line ($y = 0.0089(\pm 0.0010)x$, $R^2 = 0.81$). All calibration measurements lie above determined method LOQs for PAS and denuders (black dotted line).

indicates that assigning the origin as a known point on the chamber sampling rate curve is justified. This assertion is supported by the error associated with the least-squares intercept clearly encompassing the origin in the free form fit (Fig. 2, caption). This final form where the calibration line passes through the origin is consistent with PAS chamber calibration studies for HNO_3 that have reported PAS negative controls to be free of bias or are able to apply blank correction.[28,29,49]

Based on these justifications, the sampling rate function passing through the origin is the most representative approach for accurate analytical determinations (Fig. 2). Taking the inverse of the slope, the sampling rate for TFA is $113 \pm 12 \frac{TFA_{(g)}(ng\ m^{-3}) \times t(h)}{TFA_{(filter)}(ng)}$. This is the first nylon PAS calibrated for TFA, so we cannot compare to other studies. The coefficient of determination ($R^2 = 0.81$) indicates a strong linear response for quantifying TFA. We do not observe any suggestion that the PAS neared saturation at the upper range of these calibration levels. While saturation levels of Sartorius nylon filters have not been quantified in the current PAS, they have been characterized for Nylasorb filters (with no overlying filters) to be 5700 $\mu g\ m^{-3} \times h$ of HNO_3. This equates to 411 μg of NO_3^-,

which is more than 2 orders of magnitude higher than the amount of TFA recovered in our most concentrated extract.[29] Our PAS should have an even higher capacity, because they include thicker filters (more chemisorption sites) and an overlying filter (reduces the uptake rate of gaseous acids). Thus, we do not expect saturation to affect sampling of PFCAs on the timescales described here.

The resulting atmospheric sampling detection limit for TFA is 7 ppqv at a timescale of one week to 0.6 ppqv at a 3-month interval, and commensurately lower if deployed for a year (Section S7 and Table S4†), provided that the total burden of acids do not exceed the overall filter capacity, which varies from urban to rural environments. Given the strong acid nature of TFA ($pK_a \sim 1$), its uptake on these filters is expected to be irreversible under atmospheric conditions, as is the case for HNO_3.

3.3 Predicted sampling rate for other PFCAs

A chamber calibration using a primary gas standard for PFCAs is time consuming, making reasonable theoretical options to extend the measured TFA sampling rate to the remaining suite of PFCA homologues appealing. We considered two approaches based on our past and current work. First, we used past determinations of HNO_3 sampling rates determined under field conditions, as this would allow comparison to our measured TFA sampling rate as a secondary check on the theoretical model. Second, we used the measured TFA rate alone, as a representative member of the PFCA family in terms of molecular properties.

For both approaches, our theoretical model was based on the relative differences in known molecular diffusion properties of two test molecules. Molecular effusion is the central principle of the PAS collection strategy, leading to the diffusion coefficient-driven uptake of the target PFCAs on the nylon substrate. We considered two frameworks of differing degrees of complexity and therefore accuracy, which were Graham and Fuller's Laws (eqn (S2), (S3), Table S6 and Section S8†) to assess a relative rate of effusion based on molecular mass alone, or in combination with molecular volume, respectively.

In the first approach, the prediction of the TFA sampling rate by Graham and Fuller's Laws using the field-derived sampling rate of HNO_3 was found to be different by 60% from the measured TFA sampling rate in our chamber experiments. A number of underlying environmental and experimental factors have potential for explaining the discrepancy and are discussed in detail in Section S8 of the ESI.† Ultimately, a relative sampling rate for PFCAs based on HNO_3 has insufficient experimental grounding to correctly predict our measured TFA sampling rate.

Therefore, in our second approach, the measured TFA sampling rate was treated as the most suitable option on which to base our theoretical determination for $\geq$C2 PFCAs. Using TFA as a reference also ensures that the target molecules under consideration are all within the same chemical family – consisting of a hydrophobic tail and hydrophilic carboxylate head group. Both laws yielded similar sampling rate values for the ultra-short chain PFCAs (C2–C4) while the longer chained PFCAs yield higher sampling rates with Fuller's Law. The

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Table 1 Sampling rates $\frac{PFCA_{(g)}(ng\ m^{-3}) \times t(h)}{PFCA_{(filter)}(ng)}$ of individual PFCAs and HNO$_3$. The HNO$_3$ sampling rate was obtained from outdoor inter-comparison (Section S3), while that for TFA was measured by calibration. The predicted sampling rates were determined using Graham's and Fuller's Laws and the measured TFA sampling rate

Compound	PFCA carbon number	Measured rate	Predicted rate		
			Graham's law	Fuller's law	% Difference
HNO$_3$	—	136 ± 51	—	—	—
TFA	2	113 ± 12	—	—	—
PFPrA	3	—	136 ± 14	139 ± 15	2%
PFBA	4	—	155 ± 16	161 ± 17	4%
PFPeA	5	—	172 ± 18	180 ± 19	4%
PFHxA	6	—	188 ± 20	197 ± 21	5%

difference is due to the inclusion of molecular volumes in Fuller's method, which diverges from using only relative mass to estimate relative diffusion for larger molecules in Graham's Law. The sampling rate discrepancy for the longest homologue detected in our ambient work, PFHxA, has a 5% larger predicted value using Fuller's Law (Table 1). Evidence that Fuller's Law is better at predicting diffusion rates of organic molecules has been reported.[50–52] Gu *et al.*,[50] in particular, demonstrated Fuller's Law to predict diffusivities of halogenated organic gasses very well when compared with measured values. Some of the molecules tested included fluorinated compounds such as CH$_2$F$_2$ (HFC-32), hexafluorobezene, and 1-fluorohexane, where the difference between the predicted and measured values were ≤9%. Since PFCAs are organic halogenated molecules, Fuller's Law is better suited for predicting their relative diffusion rates to TFA – and by extension their sampling rates.

While homologues beyond PFHxA were not detected in our ambient samples (Section 3.4), the phase distribution of longer chain PFCAs (C7–C14) is not well established,[15] and we provide sampling rate predictions for these molecules in Table S6.† Given the very similar physical properties of our PFCA analyte suite, this method is the first to yield a quantitative passive sampling approach that is selective for PFCAs. Uncertainties in these measurements will stem from the variability in the underlying calibration data, although systematic errors have been minimized as much as possible through the chamber experiments with TFA and recovery QA/QC work for the entire analyte suite.

Use of these predicted sampling rates should provide mixing ratios accurate within an order of magnitude or better for these other PFCA homologues. Greater certainty at this time is not possible, due to the lack of established validated atmospheric sampling methods[53] with which to intercompare our method. This theoretical approach also opens the door to estimating atmospheric levels of other volatile acidic PFAS and haloacetic acids that have similar structural features to TFA and no established gas phase calibration methodology (*e.g.*, perfluoroalkyl sulfonic acids, Gen-X, *etc.*).

3.4 Measurement of ambient air

Measurements of gaseous PFCAs were performed in three different areas of Canada over the course of approximately one year (Fig. 3). To determine mixing ratios, we used the calibrated sampling rate of TFA and the Fuller's Law sampling rates for the C3 to C6 PFCAs. Detection limits vary based on deployment time and analytical method. For an 8-week deployment—similar to the shortest time frame considered here—LODs for PFCAs analyzed using IC-MS (Table S4†) ranged from 0.3 to 1.6 parts-per-quadrillion mixing ratios (10^{-15} mol mol^{-1}, ppqv) which are equivalent to mass loadings of 3.6 to 15 picograms per cubic metre of air (pg m^{-3}). Despite mass loadings being commonly used to set exposure limits, they are dependent on homologue molecular weight. We consider mixing ratios to be more informative for our discussion when evaluating relative atmospheric abundance and processes governing the formation and fate of PFCAs. In all PAS, TFA was detected, while PFPrA, PFBA, PFPeA, and PFHxA were detected in 86, 93, 57, and 21% of samples, respectively.

The relative mixing ratios of PFCAs generally decrease with increasing chain length, with TFA substantially higher than other PFCAs. Levels of TFA ranged from 11.0 to 200 ppqv, while all other PFCAs were between 0.2 and 26.4 ppqv (Fig. 3 and Table S3†). As expected, when atmospheric mixing ratios approached the method detection limits (Table S4†) for the sampling timescale and analytical technique, the variability within the replicate samples increased beyond 30% (Table S3†). Given the extremely low levels quantified, this level of uncertainty at <10 ppqv mixing ratios is reasonably acceptable. The inverse relationship between chain length and mixing ratios is generally consistent with relative levels of PFCAs reported in atmospheric deposition and for air measurements,[11,21–25] as well as those predicted by a model of atmospheric degradation of PFAS precursors.[13] This relative abundance of PFCAs is consistent with known sources, as the number of potential atmospheric precursors increases with decreasing chain length.[5,13] This is especially true for TFA, which can be formed from PFAS precursors, as well as numerous heat transfer fluids.[5,54]

Samples in Toronto and Tadoussac were collected with sufficient temporal resolution to observe seasonal differences. In both locations, we observed that TFA mixing ratios were higher in the summer and lower during the winter. This seasonal trend for gaseous TFA has previously been observed in Toronto[24,36] and elsewhere.[55–57] Seasonal differences for TFA have been attributed to increased photochemical activity in

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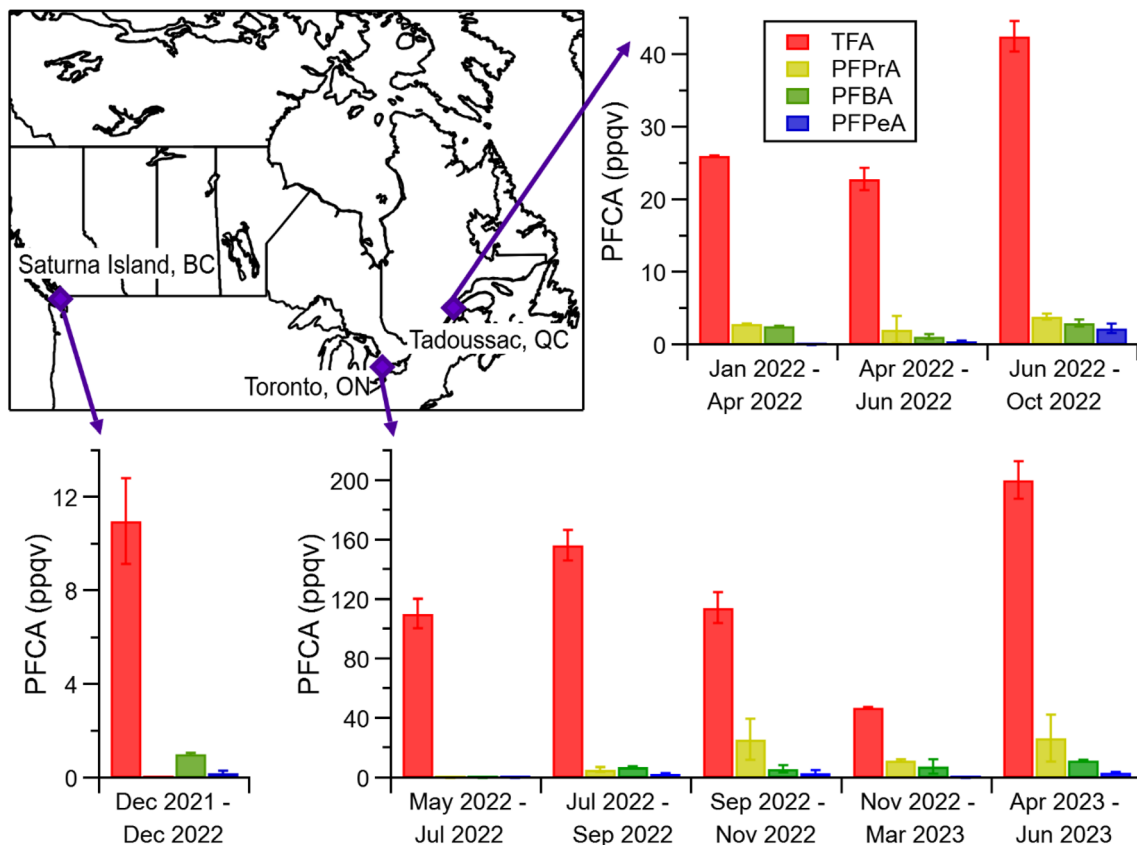This journal is © The Royal Society of Chemistry 2025

Fig. 3 Measured mean PFCA mixing ratios (ppqv) for TFA (C2), PFPrA (C3), perfluorobutanoic acid (PFBA, C4), and perfluoropentanoic acid (PFPeA, C5) from three locations in Canada: Saturna Island, BC, Toronto, ON (York University site), and Tadoussac, QC. Error bars show relative error ($n = 2$) and one standard deviation of replicate ($n \geq 3$) samples. PFHxA (C6) was not included because of low detection frequency. Mass loadings (units: pg m^{-3}) are provided in Table S3,† as these units are used in policy, but not informative in terms of assessing atmospheric formation and fate processes in a consistent manner across the homologue suite of PFCAs.

summer, as well as increased emissions of precursors.[24,36,58] No clear seasonal trend was observed for the other PFCAs. This similarity in mixing ratios between seasons is generally consistent with other gaseous C4–C6 PFCA measurements made in Toronto,[24,59] while we are not aware of any other measurements with which to compare our C3 data.

Potential sources of PFCAs vary between the sites sampled: Toronto is an urban area with many potential PFCA sources; Tadoussac is a rural area that is downwind of urban regions; and the sampling location on Saturna Island is a remote site planned by the Canadian Air and Precipitation Monitoring Network to receive mainly marine airmasses from the North Pacific. Gaseous TFA followed the trend of urban > rural > remote, with Toronto measurements highest and the lowest measurement on Saturna Island. This is generally consistent with the spatial trend predicted by models describing atmospheric formation of TFA from precursors.[60,61] Similarly, PFPrA was higher in urban Toronto and lowest in remote Saturna Island. The C4 to C6 PFCAs were generally higher in Toronto, but measured levels were more similar across the different areas. This is generally consistent with the spatial trend predicted from atmospheric formation of PFCAs from long-lived PFAS precursors.[13] Atmospheric gas and particle C4 to C6 PFCAs from several locations across Canada between 2015 and

2017 show higher concentrations than our gas-only measurements with similar spatial trends.[62,63]

Within Toronto, we observed that levels of TFA were higher at York University compared to the residential area located ~14 km away (Table S3†). For the single sample collected over the same time period in both locations, the TFA was 90% higher at York University (Section S7 and Fig. S9†). Another study measured TFA in Toronto during the summer of 2022 using chemical ionization mass spectrometry with acetate ionization.[24] That study measured mean (±one standard deviation) TFA of 546 (±255) ppqv over ~8 weeks a few km from York University (Fig. S9†). While this is higher than the values measured by the PAS, given the spatial and temporal variability in Toronto and measurement uncertainties, we consider these levels to be generally consistent. Other PFCAs were measured at similar levels by the PAS at the two Toronto sites.

4. Conclusion

The nylon-based PAS developed to sample atmospheric HNO$_3$ have been successfully extended for use with, and calibrated for, the collection of gaseous TFA. The calibration uses a primary gas phase standard, with a theoretical extension to estimate the sampling rates of the C3–C6 PFCA homologues. These results

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present the first ever PAS calibrated for gaseous TFA with the ability to sample the full suite of gaseous PFCAs at ultra-trace levels of parts per quadrillion by volume (ppqv, 10^{-15} mol mol^{-1}) for one week sampling durations and sub-ppqv levels at timescales of months.

Rigorous QA/QC was performed to ensure a robust methodology and therefore quantitation of TFA by both PAS and annular denuders within the calibration experiment. The QA/QC performed included intensive analysis of reagent through field blanks, spike and recovery at relevant quantities in real atmospheric samples, and inclusion of isotopically labeled internal standards to account for matrix effects and instrument drift in the analysis. Detection of the PFCA target suite was accomplished using three analytical instruments: a GC-MS and an IC-CD or IC-MS.

The PAS design was optimized based on our prior work with this analyte suite and to make the method more robust and financially accessible. We replaced the expensive PTFE overlying filter with a cheaper PP filter and found no significant changes in sampling rate and precision. The TFA sampling rate for our custom-built PAS was determined to be $113 \pm 12 \frac{\text{TFA}_{(g)}(\text{ng m}^{-3}) \times t(\text{h})}{\text{PFCA}_{(\text{filter})}(\text{ng})}$. The sampling rate for the C3–C6 PFCA homologues were predicted using Graham's and Fuller's laws based on this chamber calibration for TFA, which we expect to be accurate within an order of magnitude or better – considering the very similar physical properties and the knowledge that they are recovered from the PAS quantitatively. Of these two laws, Fuller's law is expected to be best suited for predicting the sampling rate of these organic halogenated compounds and was used to convert recovered quantities to mixing ratios of PFCAs collected from across Canada.

Atmospheric abundance by PFCA homologue showed TFA present in greatest quantity, with abundance decreasing with increasing PFCA chain length. The relative abundance between the urban, rural, and remote sampling sites reflected the known sources expected within or upwind of these sampling sites. At a seasonal scale, it was observed that TFA increased in abundance alongside known atmospheric precursor source patterns and oxidative reaction pathways of those precursors. All of these trends are consistent with expectations regarding abundance, distribution, and chemistry governing the presence of gaseous PFCAs in the atmosphere.

This novel PAS represents the first one specifically calibrated for TFA and the only PAS that is chemically selective for PFCAs. The calibration of our nylon-based PAS for TFA paves the way for measuring similar, difficult to measure, novel gaseous acidic compounds in the atmosphere while addressing limitations of previous methods, such as selectivity, dynamic range, ultra-trace detection limits, sampling site selection, labour intensity, and minimizing cost.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

The authors declare that they do not have any conflicts of interest associated with this work.

Acknowledgements

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